Objective of Presentation

- To share key learnings from
  - a potentially serious Near Miss Reactive Chemicals event
  - The Root Cause Investigation (RCI) which followed the event
Background

- Rohm & Haas plant, ~25 yrs old
- Acquired by Dow in 2009
- Makes hydroxy alkyl acrylates
  - Acrylic or Methacrylic acid
  - Ethylene or Propylene oxide
- Semi-batch process
Process

- Glacial Acrylic Acid
- Glacial Methacrylic Acid
- Catalyst
- Scrubber
- Sulfuric Acid
- Separation and Purification Process

Diagram:
- HAA Reactor
- Separation and Purification Process
- Scrubber
Catalyst Bulk Feed
Catalyst Screw Conveyor
Catalyst Drop Valve
Plug in Drop Valve
Serious Situation

• No catalyst added to reactor
• Large amount of unreacted methacrylic acid (MAA)
• Large amount of unreacted ethylene oxide (EO)
• Support team called to plant
• Reactive Chemicals expert paged at 2:00 AM
Immediate Mitigation

- EO vented to water scrubber, converted to glycol
- Nitrogen sparge helped strip EO to scrubber
- Reactor sampled after many hours of scrubbing vent
- ARC (Accelerating Rate Calorimeter) test performed to guide next steps in mitigation
Catalyzed ARC Test
Safe Conclusion of Event

- ARC analysis showed reactor cooling capable of handling remaining EO safely.
- Root Cause Investigation (RCI) conducted before restart
- Ultimately, catalyst was added to reactor and batch was completed successfully.
RCI Conducted

- Large, multi-functional team assembled due to potential severity of the event.
- Several tools employed (e.g., Cause & Effect Diagram) to thoroughly understand issues.
- Numerous opportunities for improvement uncovered
Root Causes

- Malfunction in sequencing of catalyst addition valve allowed liquid to back up into solids line
- Catalyst charging inadequate
  - Fluctuating weigh cells
  - No detection of valve plugging
- No reliable method to check catalyst concentration in reactor
- Unreacted EO protection inadequate
  - Inadequate low temperature cut-off and reactor pressure alarms
Contributing Causes

- Inadequate Management of Change (MOC)
  - Trouble-shooting guide not updated
  - Procedures not updated
- No Process Safety Cardinal Rules available
- Inadequate training on consequences of deviation from critical process parameter limits
Corrective Actions

• Critical actions were required before plant resumed operations
• Important, non-critical actions scheduled within 90 days
• Long-term improvement opportunities targeted for completion within one year
Summary of Key Learnings

• Process Hazards and mitigations must be well documented in procedures and training.
• Critical process parameters must have a reliable method or control system in place.
• Operating procedures must be up to date and MOC process must be followed.
• Abnormal situations may become accepted if they are allowed to continue for long periods.